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RESEARCH AND DEVELOPMENT

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MEMORANDUM

**SUBJECT:** Summary Report of Decatur, AL, Water Sample Analyses

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NERL scientists completed their analysis of the water samples collected by the Region 4 scientists at the three Decatur, Alabama municipal treatment plants. These samples were analyzed for PFOA, PFOS, and other selected perfluorinated compounds using a method specifically developed to support the Region 4 analyses and which has not been fully validated.

Attached is a summary report that provides the PFOA and PFOS analytical results for the grab water and quality control samples. These analytical results document that the measured PFOA and PFOS concentrations were very low (less than 0.040 parts per billion). The quality control data demonstrate that exceptional care was taken in sampling, storing, and shipping the samples. PFOA and PFOS were not measured above the method detection limit in the field and laboratory blank samples. The results from the repeated analysis of the samples (each analyzed six times) demonstrate excellent analytical precision. However, it is important to recognize that these results represent only a single

sampling event which does not capture temporal changes in water concentrations or the contribution by any particular source.

The analytical results of the other perfluorinated compounds are still being evaluated and will be reported at a later date. However, an initial review of the draft data indicates that the concentrations for these compounds, when detected, were within an order of magnitude of the PFOA concentrations.

Please contact me (919-541-2106), Linda Sheldon (919-541-2205), or Eric Weber (706-355-8555) if you have any questions.

Attachment



## Summary Report – Results of Analyses on Decatur, AL Water Samples

The following summarizes the procedures employed for collecting and analyzing the Decatur, AL water and corresponding quality control samples.

**Sample Collection:** Sampling collection materials (HDPE bottles, nitrile gloves, etc.) were rinsed 3x in methanol before the sampling trip. Water samples were collected in HDPE sample bottles after rinsing 3x in the water to be sampled. When water was collected from a flowing source, the sample was collected directly from flow. When water was collected from a pool, as opposed to flowing from a tap, for example, disposable nitrile gloves that had been rinsed 3x in methanol were donned. The samples were kept in a cooler without any cooling effort. No preservatives were used.

**Sample Preparation and Analysis:** This method was developed to support the Region 4 program and has not been fully validated. All sample preparation was performed on a mass basis for maximum accuracy. A 9.88 ml aliquot of sample was transferred to an HDPE vial. This aliquot was spiked with ~0.138 g of 96%/4% acetonitrile/water containing mass-labeled matrix internal standards at 6.1 ng/g. This treatment yielded samples consisting of about 99% water and 1% acetonitrile, by mass, containing 84 pg/g of matrix internal standards, the same concentration that the calibration standards contain. Spiked samples were transferred to polypropylene autosampler vials. All samples were analyzed by ultra-performance liquid chromatography, tandem mass spectrometry operated in negative electrospray-ionization mode. Deionized water was polished by elution through an SPE cartridge to represent zero concentration of the analytes.

PFOA was quantitated by isotopic dilution using its corresponding matrix internal standard. PFOS was quantitated using mass-labeled perfluorodecanoic acid as a matrix internal standard. Limits of quantification (LOQs) were calculated using the collected water samples and the polished deionized laboratory water. LOQs were calculated using American Chemical Society conventions (Keith et al., 1983), altered following the approach of Washington (2007) to include uncertainty imparted from background detections in blanks that commonly are encountered with these analytes. This adjustment is conservative for calculating detection limits.

**Quality Control:** Quality control samples were transported to the field and/or held at the laboratory to document any potential contamination or loss of constituent due to sample collection, transport or storage. These included:

- A clean, sealed HDPE bottle containing purified deionized water that was carried to the field but not opened.
- A clean, sealed HDPE bottle containing purified deionized water that was carried to the field where it was opened and immediately transferred to a clean, empty HDPE bottle.
- An HDPE bottle containing a field spike solution consisting of 102 pg/g (ppt) of  $^{13}\text{C}_8$ -perfluorooctanoic acid ((M+8)PFOA) in deionized water polished by elution through a solid-phase extraction (SPE) cartridge.

- A duplicate raw water sample at the Moulten, Sinking Creek location.

Laboratory quality controls and samples were prepared in replicate with each replicate spiked with matrix internal standards independently of the other to reflect variation from spiking. Each replicate was run 3 times so that each water sample was represented by six analytical runs for each analyte. Samples were interspersed with standards and blanks. Standards were run six times at each of 8 or 9 levels ranging from 0.9 pg/g to 230 pg/g.

**Results:** Only the West Morgan raw and finished water PFOA and PFOS concentrations (Table 1) were measured above the limit of quantitation. The West Morgan raw and finished water PFOA and PFOS levels were similar. However, these concentrations are very low, less than 0.040 parts per billion. The results of analysis on the field and laboratory control samples (Table 2) document that the samples were not contaminated through the sampling and storage process. The recovery of PFOA in the spike sample documents sample integrity over the sampling/analysis time period. The coefficient of variation of the samples exceeding the limit of quantitation was  $\leq 22\%$ , and demonstrates excellent method repeatability.

#### References:

Keith, LH, Libby, RA, Crummett, W, Taylor, JK, Deegan, Jr., J, Wentler, G. 1983. Principles of environmental analysis. *Analytical Chemistry*. 55. 2210-2218.

Washington, JW, Ellington, JJ, Jenkins, TM, Evans, JJ. 2007. Analysis of perfluorinated carboxylic acids in soils: Detection and quantitation issues at low concentrations. *Journal of Chromatography A*. 1154. 111-120.



**Table 1. Analytical Results for Decatur, AL Municipal Water Samples**

MUNICIPAL PLANT	PLANT ID	WATER SAMPLE	SAMPLE TYPE	PFOA	PFOS
Moulton Turkey Creek	PWS01	Raw	Primary	< <sup>a</sup>	< <sup>b</sup>
Moulton Sinking Creek	PWS02	Raw	Primary	<	<
			Duplicate	<	<
		Finished	Primary	<	<
West Morgan East Lawrence	PWS06	Raw	Primary	28 ppt	26 ppt
		Finished	Primary	25 ppt	21 ppt
		Finished	Plant Kitchen	26 ppt	<
Decatur	PSW08	Raw	Primary	<	<
		Finished	Primary	<	<

<sup>a</sup> Less than the PFOA method limit of quantitation (10 ppt)

<sup>b</sup> Less than the PFOS method limit of quantitation (19 ppt)

**Table 2. Analytical Results for Quality Control Samples**

SAMPLE TYPE	HOW PROCESSED	PFOA	PFOS
Laboratory Water	Tap	< <sup>a</sup>	< <sup>b</sup>
Collection Container filled with Laboratory Water	Not Opened in Field	<	<
	Opened in Field	<	<
	Held at Athens Lab	<	<
Collection Container filled with Laboratory Water and Spiked with PFOA (102 ppt)	Not Opened in Field and Spiked with mass labeled PFOA	108 ppt	<

<sup>a</sup> Less than the PFOA method limit of quantitation (10 ppt)

<sup>b</sup> Less than the PFOS method limit of quantitation (19 ppt)